

PATENT SPECIFICATION

(11)

1 320 134

DRAWINGS ATTACHED

1 320 134

(21) Application No. 42714/69 (22) Filed 27 Aug. 1969

(19)

(23) Complete Specification filed 19 Aug. 1970

(44) Complete Specification published 13 June 1973

(51) International Classification C02B 1/12

(52) Index at acceptance

C1C 20X 302 404 40X 424 426 435 61X

(72) Inventors DAVID ARTHUR WEBBER and WILLIAM MOLNAR



(54) PURIFICATION OF WATER AND NATURAL GAS

- (71) We, CRYOPLANTS LIMITED, a British company, of Hammersmith House, London, W.6, 9DX, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a purification process and more particularly to purifying water and natural gas.
- A cheap and effective method for producing potable water from sea water or other brackish waters has long been sought. Distillation is widely used but its fuel and equipment requirements are costly. Numerous chemical treatments of sea water for producing potable water or salt concentrate have also been proposed, involving the addition of reagents to react with the impurities to form products readily separable from the water. These chemical treatments are also costly and have chiefly been used for the small-scale production of potable water from sea water.
- It has been proposed to desalinate water by continuously reacting salt water with a hydrate-forming gas to form solid hydrates, washing the solid hydrates to remove adhering salt and other impurities, decomposing the solid hydrate to form a potable water product and hydrate-forming gas and recycling the hydrate forming gas to recontact the salt water. Carbon dioxide, methane, ethane, propane, n-butane, isobutane and certain fluorinated hydrocarbons have been proposed as suitable hydrate forming substances. For such a cyclic process, as has been proposed, propane and certain fluorinated hydrocarbons have been found to be the most suitable hydrate forming substances. Methane is readily available but requires to be subjected to a relatively high pressure to form solid hydrates.
- Natural hydrocarbon gas, which contains a high proportion of methane, is generally available at high well head pressures and many sources of such natural gas exist in or close to areas having insufficient supplies of potable water. It is often required to liquefy natural hydrocarbon gas for storage and transportation and before such liquefaction it is necessary to remove deleterious substances, such as high melting point hydrocarbon impurities. The present invention relates to a method for purifying water, utilising a supply of natural hydrocarbon gas, which simultaneously removes such impurities from the natural hydrocarbon gas. The term "natural gas feedstock" as employed herein refers to a gaseous mixture of hydrocarbons obtained from a naturally occurring hydrocarbon gas mixture and including as impurities hydrocarbons having six or more carbon atoms in the molecule but free from deleterious non-hydrocarbon impurities such as sulphur compounds.
- The present invention accordingly provides a process for simultaneously purifying both water and natural hydrocarbon gas which includes reacting an impure water feedstock with a natural gas feedstock (as hereinbefore defined) to form solid hydrocarbon hydrates and a water residuum having an enhanced content of impurities from the feedstocks, separating the solid hydrates from the water residuum, washing the solid hydrates with an aqueous medium having a lower concentration of impurities than the water residuum so as to remove adhered impurities from the solid hydrates and thereafter decomposing the washed hydrates to form purified water and purified gaseous hydrocarbon product.
- In order to form sufficient quantities of solid hydrocarbon hydrates it is generally necessary for the natural hydrocarbon gas and water to be reacted at superatmospheric pressure. Preferably the superatmospheric pressure is obtained by utilising the available well head pressure of the natural hydrocarbon gas. This well head pressure which is generally of the order of 2000 to 4000 psi may also if desired be used to generate electrical or mechanical power, for example to supplement the power requirements of the process.
- Although the separation and washing of

the solid hydrates can be effected in a single step, the solid hydrates are preferably at least partially separated from the impure water residuum before the washing step.

Such separation can be by sedimentation, filtration or centrifuging. Continuous filtration may be effected by a drum filter disposed between the reaction vessel and the washing stage. Washing of the solid hydrates may be effected in a plurality of steps and the initial washing step may be carried out using an impure washing medium having the same composition as the feedstock water.

The hydrates can be decomposed either by heat or by expansion to a low pressure. Preferably at least some of the heat of reaction, evolved on formation of the solid hydrates may be decomposed by a separate heating medium, such as steam.

The impure water residuum may be recycled and recontacted with further natural hydrocarbon gas, or it may be subjected to further purification stages. Purification in the further purification stages may be effected by a method according to the present invention.

The natural gas feedstock may also contain added hydrate forming substances. For example, part of the purified gaseous hydrocarbon product may be added to the natural gas feedstock or the hydrocarbon product may be used as a hydrate forming gas in the further purification stages.

The water produced on decomposition contains a reduced amount of impurities, the concentration of which depends on the efficiency of the washers, the purity of the washing media and the extent to which impure liquid is removed after each stage in the process.

By controlling these conditions it is possible for the fraction to be sufficiently pure to be potable.

The invention will now be described by way of example and with reference to the accompanying drawing which is a diagrammatic representation of a plant for desalinating water.

As shown in the drawing, natural gas at the available well head pressure is passed via a conduit 1 into a prepurification plant 2, wherein sulphur compounds are removed, to form a natural gas feedstock which is introduced into a reaction vessel 4 via an inlet conduit 6. Feedstock sea water is compressed to the well head pressure of the natural hydrocarbon gas by a compressor 3 and is passed to a hydrate reaction vessel 4, via an inlet conduit 5, wherein it reacts with the natural gas.

Components of the natural gas, in particular methane, ethane, propane and butane, react with the water to form solid hy-

drates and an impure water residuum having an increased salt content. The concentrated salt water residuum and any gas that has not reacted is passed to a gas/liquid separator 7 via an outlet conduit 30. The liquid from the separator 7 is passed to a liquid/liquid separator 8 wherefrom an upper and lower liquid fractions are removed. The lower liquid fraction comprises mainly concentrated salt water and may either be discarded or passed through further desalination processes to extract further quantities of potable water. The upper fraction from the separator 8 contains mainly liquid hydrocarbons.

The solid hydrates and some concentrated salt water residuum separate from the bulk of the concentrated salt water by sedimentation and are removed from the reaction vessel 4 in the form of a slurry via an outlet conduit 31. The slurry is passed to a first washer 9 and thence to a second washer 10. The washed hydrate slurry is then passed to a decomposition vessel 11. The decomposition vessel 11 is provided with heating coils 12 and 13 which serve to raise the temperature of the hydrate above its decomposition temperature thereby forming a mixture of gaseous hydrocarbons, and water.

The heating coil 12 is heated by steam and the heating coil 13 is heated by a heating medium pumped through conduits 14 and 15 by a pump 16, the heating medium having been heated in the coil 17, disposed within the reaction vessel 4, by the heat of reaction of the natural hydrocarbon gas and water.

The gaseous hydrocarbon product contains mainly methane, ethane, propane and butane, the bulk of the high melting point hydrocarbon impurities having been removed from the apparatus as the upper fraction in the separator 8. A portion of the gaseous hydrocarbon product may optionally be added to the pre-purified natural hydrocarbon gas feedstock by a gaseous product recycle conduit 18. At least the major portion of the gaseous hydrocarbon product, however, is removed via a conduit 24. It may either be expanded through an expansion turbine (not shown) to the required distribution pressure, or may be removed at well head pressure for liquefaction and storage.

A portion of the water product is returned by pumps 19 and 20 through the washers 10 and 9 to provide washing therein, the washing water from washer 9 being returned by a pump 21 to the reaction vessel 4.

The major portion of liquid removed from the decomposition vessel 11 is expanded through an expansion valve 22 and passed to a gas/liquid separator 23. The gaseous fraction removed from the separa-

70

75

80

85

90

95

100

105

110

115

120

125

130

BEST AVAILABLE COPY

3

1,320,134

3

tor 23 may either be burnt to provide steam
for the heating coil 12 or compressed and
added to the gas leaving conduit 24. The
purified water is withdrawn through conduit
5 25.

WHAT WE CLAIM IS:—

1. A process for simultaneously purify-
ing both water and natural hydrocarbon gas
which includes reacting an impure water
10 feedstock with a natural gas feedstock (as
hereinbefore defined) to form solid hydro-
carbon hydrates and a water residuum hav-
ing an enhanced content of impurities from
the feedstocks, separating the solid hydrates
15 from the water residuum, washing the solid
hydrates with an aqueous medium having a
lower concentration of impurities than that
of the water residuum to remove adhered
impurities from the solid hydrates and there-
20 after decomposing the washed hydrates to
form purified water and purified gaseous
hydrocarbon product.

2. A process according to claim 1,
wherein superatmospheric pressure for the
25 reaction is obtained by utilising the avail-
able well head pressure of the hydrocarbon
gas.

3. A process according to claim 1 or
claim 2, wherein the solid hydrates are at
30 least partially separated from the impure
water residuum before washing.

4. A process according to any preceding
claim, wherein the solid hydrates are separ-

ated from the impure water residuum by
sedimentation.

5. A process according to any one of
claims 1 to 3, wherein the solid hydrates
are separated from the impure water resi-
duum by continuous filtration using a drum
filter disposed between a vessel in which the
reaction is effected and a vessel in which
the washing is effected.

6. A process according to any preceding
claim wherein the washing is effected in a
plurality of steps and the initial washing step
uses an impure washing medium having the
same composition as the feedstock water.

7. A process according to any preceding
claim, wherein the solid hydrates are de-
composed by heat.

8. A process according to claim 7,
wherein at least some of the heat of reac-
tion evolved on formation of the solid hy-
drates is utilised to decompose them.

9. A process according to any preceding
claim wherein the natural gas feedstock also
contains added hydrate-forming substances.

10. A process according to claim 9
wherein the added hydrate-forming sub-
stances are part of the purified gaseous
hydrocarbon product.

11. A process according to claim 1 sub-
stantially as described herein with reference
to the drawing.

For the Applicants,
F. W. B. KITTEL,
Chartered Patent Agent.

BEST AVAILABLE COPY

1320134

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

